POSSIBLE NONURBAN ENVIRONMENTAL EFFECTS DUE TO CARBON MONOXIDE

AND NITROGEN OXIDES EMISSIONS

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INTRODUCTION

During the last few years, the nonurban environmental effects of carbon monoxide (CO) and nitrogen oxides (i.e., NO_x = NO + NO_2) emissions have been investigated by an increasing number of people (e.g., Crutzen (ref. 1), Sze (ref. 2), Chameides et al. (ref. 3), Stewart et al. (ref. 4), and Liu (ref. 5)). In this paper, these environmental effects which have been investigated will be reviewed and some new effects explored. Also, the sources and sinks of NO_x and its concentrations in the troposphere will be discussed in detail. Only a brief discussion of the sources and sinks of CO will be given here since there are already excellent discussions on this subject (Seiler (ref. 6), Jaffe (ref. 7), and Crutzen and Fishman (ref. 8)).

SOURCES, SINKS, AND CONCENTRATIONS OF NO_x

Nitric oxide (NO) is usually produced during high-temperature combustion. When No is released into the atmosphere, it is quickly converted to NO_2 through the reaction,

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{1}$$

This conversion gives NO a lifetime of about 100 seconds in the clean troposphere. Most of the NO_2 produced is photolyzed back to NO, but some recombines with OH to give HNO_3, which is scavenged by rain. The sources and sinks of NO_x are very uncertain. Table I lists the possible sources and sinks. The anthropogenic source, the only well-known one, contributes about 10 million metric tons of nitrogen per year (10 Mt(N)/yr) from automobiles and another 10 Mt(N)/yr from industrial sources, mainly power plants. The stratospheric downward flux of NO_x is calculated from a one-dimensional model. Its source is oxidation of N_2O by $O(^1D)$ in the stratosphere. Production of NO_x from the reaction of NH_3 with OH is very uncertain because the average concentration of NH_3 is not known. Measurements in the clean rural area are scarce (Georgii and Müller (ref. 9) and Lodge et al. (ref. 10)). However, the average concentration of NH_3 in the troposphere can be estimated if its source and

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lifetime are known. Dawson (ref. 11) estimated the source of NH_3 to be about 50 Mt(N)/yr. Since NH_3 is easily scavenged by rain droplets and absorbed by plants and soil, its lifetime can be assumed to be less than 5 days. If the average OH concentration is assumed to be 4×10^5 cm^{-3} (Singh (ref. 12)), then the lifetime for NH_3 oxidation by OH is about 180 days. Therefore, less than 3 percent of the NH_3 will be oxidized by OH; that is, the upper limit of this source of NO_x is 2 Mt(N)/yr. The most important natural source of NO_x is probably lightning. Noxon (ref. 13) measured enhancements of NO_2 during a number of storms and gave an order-of-magnitude estimate of a global source of NO_2 from lightning of about 10^{10} cm^{-2}-sec^{-1} or 40 Mt(N)/yr. Recent theoretical calculations (Griffing (ref. 14)) have arrived at somewhat the same order of magnitude for production of NO_2 in lightning. Since there is probably as much NO produced in lightning (Griffing (ref. 14), Chameides et al. (ref. 15), and Tuck (ref. 16)), the total NO_x source due to lightning is about 80 Mt(N)/yr. This value is probably too high because the ultimate sink of NO_x is the soil and ocean, where it is converted to nitrate. This source strength implies that a substantial amount of fixed nitrogen nutrient is input into the soil and ocean. The natural nitrogen fixation rate is only about 175 Mt(N)/yr on the land (Hardy and Havelka (ref. 17)) and only about 10 Mt(N)/yr in the ocean (Delwiche (ref. 18)). How much NO_x is produced from forest fires and agricultural burning is uncertain; however, if it is assumed that the emission efficiency is the same as for coal burning, this source can be estimated to be less than 10 Mt(N)/yr.

The sinks of NO_x are very uncertain except for the photochemical sink,

$$OH + NO_2 + M \rightarrow HNO_3 + M \tag{2}$$

The averaged tropospheric OH concentrations, 2×10^5 cm^{-3} in the Northern Hemisphere (N.H.) and 6×10^5 cm^{-3} in the Southern Hemisphere (S.H.), have been deduced by Singh (ref. 12) by examining the global budget and measured distribution of methyl chloroform (CH_3CCl_3). By adopting his values, the average lifetime for NO_x due to this reaction is calculated to be 2 days in the S.H. and 6 days in the N.H. Since NO_2 is soluble in water and must therefore be subject to rain scavenging, the lifetime of NO_2 against rain scavenging can be assumed to be 6 days, the same as the lifetime of water vapor. This implies that the lifetime of NO_x is about 10 days since the NO_2 to NO_x ratio is about 2 to 3. The dry deposition lifetime for NO_x is calculated from an arbitrarily assumed deposition velocity of 0.1 cm-sec^{-1} for NO_2.

Until recently, there were very few measurements of NO_x in the nonurban areas. Table II was adopted from the summaries of NO and NO_2 measurements by Drummond (ref. 19) and Noxon (ref. 20) who cite references 10 and 21 to 31. Most of these measurements were taken at one location for a short period of time with the exceptions of Noxon (ref. 20) and Lodge et al. (ref. 10). Since the lifetime of NO_x is only about 4 days, the standard deviation of its mixing ratio in the troposphere should be about 10, according to Junge (ref. 32), and even larger near the Earth's surface which is closer to the sources and sinks. Therefore, a large amount of data spread over a wide range of areas is needed to establish the average NO_x content in the troposphere. Nevertheless, in table II, one can see that very low concentrations ($\lesssim 0.1$ ppb) of NO and NO_2

have been indicated by recent measurements. Noxon, in particular, has monitored NO_2 at the National Oceanographic and Atmospheric Administration's Fritz Peak Observatory in Colorado since fall 1974 (ref. 30) and has made numerous observations over North America and Peru (ref. 20). His data have convincingly shown that in the Western Hemisphere (W.H.), the clean air tropospheric column density of NO_2 is below 5×10^{14} cm^{-2}. If the scale height of NO_2 is assumed to be about 2 km, as suggested in some recent models (Chameides (ref. 33), Crutzen et al. (ref. 34), and Liu (ref. 5)), this column density of NO_2 corresponds to a mixing ratio of only 0.1 ppb at the Earth's surface.

However, if 95 percent of the industrial NO_x and 50 percent of the NO_x from lightning are assumed to be emitted into the Northern Hemisphere, a simple one-dimensional model (e.g., Fishman and Crutzen (ref. 35), Liu (ref. 5), or Chameides (ref. 36)) would give a mixing ratio of 0.5 ppb for NO_2 and 0.2 ppb for NO at the surface. These values are 5 times higher than the upper limit set by Noxon's NO_2 observations and about 10 times higher than Drummond's NO measurements. Crutzen (private communication, 1977) suggested that there might be some as yet unknown mechanisms for removal of NO_x that is more than 5 times as efficient as the sink of reaction (2). On the other hand, Chameides (ref. 36) suggested that for a rural area which is far away from NO_x sources, the NO_x observed is probably due to the photolysis of HNO_3 because HNO_3 has a longer lifetime than NO_x. Therefore, one can assume that HNO_3 is emitted into the atmosphere instead of NO_x. The NO_x mixing ratio evaluated in this way does fall below the observed upper limit. However, more realistic multi-dimensional models are needed to verify this concept, and more measurements of NO_x, especially of the height profiles, are needed to establish the NO_x content in the troposphere.

SOURCES, SINKS, AND CONCENTRATIONS OF CO

A detailed discussion on this subject was given by Seiler (ref. 6). More detailed discussion on the anthropogenic sources of CO and its concentrations in the urban area was given by Jaffe (ref. 7). In table III, their values are given with modifications only to the photochemical source of CO from methane (CH_4) oxidation and the sink of CO due to oxidation by OH. These were calculated by using the averaged OH densities given by Singh (ref. 12) for the two hemispheres and the CO distributions given by Seiler (ref. 6). These estimates agree with an earlier study by Crutzen and Fishman (ref. 8). The sink of CO due to oxidation by OH is much larger because of the reaction,

$$CO + OH \rightarrow CO_2 + H \tag{3}$$

for which the pressure-dependent rate has been recently measured by Cox et al. (ref. 37), Sie et al. (ref. 38), Chan et al. (ref. 39), and Perry et al. (ref. 40). In the troposphere, this rate is about twice that previously accepted (Hampson and Garvin (ref. 41)). The imbalance of the source and the sink of CO is so large that there has to be an important unknown source of CO, as suggested by Crutzen and Fishman (ref. 8).

The average concentration of CO in the N.H. (0.2 ppm) is about a factor of 4 higher than in the S.H. (0.05 ppm), as shown by Seiler (ref. 6). Most

of this difference can probably be attributed to the fact that 95 percent of the anthropogenic sources of CO emitted are in the N.H.
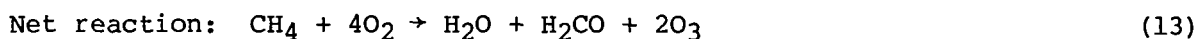
POSSIBLE EFFECTS DUE TO CO AND NO_x EMISSIONS

Increase in Tropospheric Ozone

This problem has been studied by many investigators (e.g., Chameides and Stedman (ref. 42), Stewart et al. (ref. 4), Fishman and Crutzen (ref. 35), and Liu (ref. 5)). The mechanism of production of ozone is a catalytic cycle:

$$CO + OH \rightarrow CO_2 + H \tag{3}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{4}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{5}$$

$$NO_2 + h\nu \rightarrow NO + O \tag{6}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{7}$$

Net reaction: $\quad CO + 2O_2 \rightarrow CO_2 + O_3 \tag{8}$

This is a very efficient catalytic cycle. The only weak link before was reaction (5), for which the reaction rate was accepted to be 4×10^{-13} cm^3-sec^{-1} (Hampson and Garvin (ref. 41)) but has since been measured accurately to be 8×10^{-12} cm^3-sec^{-1} (Howard and Evenson (ref. 43)). Reactions (3) and (4) can be replaced with a methane oxidation chain:

$$CH_4 + OH \rightarrow CH_3 + H_2O \tag{9}$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \tag{10}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{11}$$

$$CH_3O + O_2 \rightarrow H_2CO + HO_2 \tag{12}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{5}$$

$$2(NO_2 + h\nu \rightarrow NO + O) \tag{6}$$

$$2(O + O_2 + M \rightarrow O_3 + M) \tag{7}$$

Net reaction: $\quad CH_4 + 4O_2 \rightarrow H_2O + H_2CO + 2O_3 \tag{13}$

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Further reactions of H_2CO will produce CO. Without the anthropogenic emissions, the CO mixing ratio was probably less than 0.03 ppm, since most of the CO was produced from methane oxidation. The catalytic ozone production should have been dominated by the methane oxidation chain, reaction (13). With the present averaged CO concentration, reaction (8) now dominates the catalytic ozone production.

Anthropogenic NO_x emissions will speed up reaction (5) and thus increase ozone production rate. As discussed before, the natural NO_x source is very uncertain. Nevertheless, if the values in table I are adopted and NO_x distributions are assumed to be consistent with Noxon's upper limit on NO_2, an upper limit for ozone increase is about 40 percent in the N.H. and negligible in the S.H. These estimates can only be regarded as qualitative because of the neglect of some important nonlinear effects, such as the large deviations in water vapor and NO_x distributions. The ozone production rate has been found to increase less than linearly with NO_x, especially when NO_x concentration is higher than 1 ppb.

There are some experimental data (Fishman and Crutzen (ref. 44)) which indicate that the ozone concentration in the N.H. is about 50 percent higher than in the S.H. Of course, this could just be coincidental and the different ozone concentrations in the N.H. and S.H. could be due to other mechanisms, such as dynamics.

Stratospheric Ozone Increase

Mechanism (8) may increase the lower stratospheric ozone when tropospheric CO is transported above the tropopause. In the stratosphere, the NO_x is produced from oxidation of N_2O by $O(^1D)$. Tropospheric NO_x does not penetrate into the stratosphere because of its small scale height, as discussed before. One-dimensional model calculation shows that the northern stratospheric ozone column density is increased by about 1 to 2 percent because of CO emission. Locally, the increase in ozone can be as high as 15 percent near the tropopause. However, Seiler's (ref. 6) CO measurements just above the tropopause seem to indicate very little penetration of tropospheric CO into the stratosphere. More measurements and multidimensional calculations are needed to resolve this problem.

Effects on Tropospheric OH

The important role that the OH radical plays in the tropospheric self-cleansing processes of gases such as NO_2, SO_2, H_2S, CO, CH_4, RH, and $CH_xCl_yF_z$ has long been appreciated (Levy (ref. 45) and McConnell et al. (ref. 46)). Wofsy (ref. 47) noted that an increase in the global CO concentration may decrease the tropospheric OH concentration since CO and CH_4 are major sinks of OH. Sze (ref. 2) and Chameides et al. (ref. 3) have shown that CH_4 may increase by as much as 40 percent by the year 2000 if the anthropogenic emissions of CO keep increasing. In fact, Sze (ref. 2) has shown that CH_4 may be already increased by 20 percent since 1950. If the OH concentrations (6×10^5 and 2×10^5 cm^{-3}) in the S.H. and N.H. deduced by Singh (ref. 12) are assumed

to represent unperturbed and perturbed conditions, respectively, they imply a 33-percent decrease in globally averaged OH concentration. This corresponds to a 33-percent increase in CH_4 concentration, slightly higher than Sze's calculation. These calculations assumed a constant CH_4 source which may have increased because of human activities, according to Crutzen (ref. 48).

Emissions of NO_x can increase the tropospheric OH concentrations through reaction (5) (Liu (ref. 5)). Like the tropospheric ozone increase problem, a quantitative estimate depends on the knowledge of the background NO_x abundance and natural NO_x source. Using the values in table I and assuming NO_x to be consistent with the upper limit of Noxon's measurement, an upper limit is estimated to be a 25-percent increase in tropospheric OH concentration due to NO_x emissions. Here again, note that the nonlinear effect of large spatial deviations in NO_x concentrations is not included. This effect tends to diminish the increase of OH due to NO_x emissions.

Increases in CH_4, CH_3Cl, CH_3CCl_3, and other hydrocarbons due to decrease in OH not only could perturb the stratospheric photochemistry of odd hydrogen but also could increase the amount of odd chlorine released in the stratosphere by these species and thus further reduce stratospheric ozone (McConnell and Schiff (ref. 49)). Furthermore, the greenhouse effect of these species will be enhanced and result in a perturbation of the climate.

Acid Rain

Likens (ref. 50) has shown that the pH of precipitation in the United States and Western Europe has been dropping significantly during the last 30 years. Sulfuric and nitric acids are major sources of acidity in precipitation. The Hubbard Brook Experimental Forest in the White Mountains of New Hampshire provides the longest known record for pH of precipitation in the United States. Likens found that, although sulfuric acid had been the dominant acid in precipitation there, the increased deposition of hydrogen ions has been due primarily to the increased amounts of nitric acid in the rain and snow. It is reasonable to believe that the increase in nitric acid in the precipitation is the result of anthropogenic NO_x emissions. In Scandinavia, it has been shown that, as the acidity of precipitation increased, the number of barren lakes increased sharply. In addition, the increased acidity enhances the weathering and erosion of buildings and materials.

Fertilizer

As mentioned before, the NO_x emissions will eventually be rained out and deposited in the land and ocean as nitrate. The industrial nitrogen fertilizer production is only about 40 Mt(N)/yr (Hardy and Havelka (ref. 17)), about twice as much as NO_x emissions. Therefore, the NO_x emissions represent an important amount of fixed nitrogen fertilizer. Since nitrogen is one of the limiting nutrients in the land and ocean, it should help increase the productivity of plants. In this respect, NO_x emissions may play a positive role. However, increased fixed nitrogen input into the soil may increase the denitrification

rate and thus increase the N_2O flux into the atmosphere (Crutzen (ref. 51), Crutzen (ref. 52), McElroy et al. (ref. 53), Liu et al. (ref. 54), and Sze and Rice (ref. 55)). Increase in N_2O not only could perturb the ozone layer but also could have an increased greenhouse effect on the climate. Furthermore, increased nitrogen nutrient input into aquatic systems may speed up the rate of eutrophication of rivers and lakes.

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TABLE I.- SOURCES AND SINKS OF TROPOSPHERIC NO_x

Sources, Mt(N)/yr:
Anthropogenic   20
Stratospheric downward flux 0.5
NH_3 + OH . . . .   <2
Lightning . . . .   ≈80
Forest fires . . . .   <10

Sinks, lifetime against sink:
NO_2 + OH . . . . [a]2 to 6 days
Rain out . . . .   10 days
Dry deposition . . . .   30 days

[a]The lifetime was calculated to be 2 days in the Southern Hemisphere and
6 days in the Northern Hemisphere. See the discussion in text.

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TABLE II.- SUMMARY OF NO AND NO_2 MEASUREMENTS

[Adopted from Drummond (ref. 19) and Noxon (ref. 20)]

Gas	Amount, ppb	Location	Reference
NO_2	0.02 to 0.3	Ireland	Reference 21
NO_2	1 to 2	Florida; Hawaii	Junge (ref. 22)
NO_2	0.9 to 3.6	Panama	Lodge and Pate (ref. 23)
NO_2	4.6	North Carolina	Kronreich et al. (ref. 24)
NO_2	4.1	Pikes Peak, Colorado	Hamilton et al. (ref. 25)
NO	2.7	Pikes Peak, Colorado	Hamilton et al. (ref. 25)
NO_2	0.5 to 4		Hidy (ref. 26)
NO	0.2 to 2		Hidy (ref. 26)
NO_2	1 to 3	Central United States	Breeding et al. (ref. 27)
NO_2	4 to 21	Southern England	Nash (ref. 28)
NO_2	0.2 to 0.7	Tropics	Lodge et al. (ref. 10)
NO	0.1 to 0.7	Tropics	Lodge et al. (ref. 10)
NO_2	0.1 to 0.3	Boulder, Colorado	Moore (ref. 29)
NO_2	<0.1	Fritz Peak, Colorado	Noxon (ref. 30)
NO	$\lesssim$0.05	8 to 12 km over Pacific Ocean	Briehl et al. (ref. 31)
NO	0.01 to 0.05	Laramie, Wyoming	Drummond (ref. 19)
NO_x	0.1 to 0.4	Laramie, Wyoming	Drummond (ref. 19)
NO_2	$\lesssim$0.1	North America; Peru	Noxon (ref. 20)

TABLE III.- SOURCES AND SINKS OF TROPOSPHERIC CO

[Mostly adopted from Seiler (ref. 6) and Jaffe (ref. 7)]

	Northern Hemisphere	Southern Hemisphere	Global
Sources, Mt(N)/yr:			
Anthropogenic	450	50	500
Ocean	40	60	100
Forest fires	40	20	60
Oxidation of hydrocarbon	40	20	60
Oxidation of CH_4	80	240	320
Total	650	390	1040
Sinks, Mt(N)/yr:			
Upward flux into stratosphere	90	20	110
Uptake by soil	300	150	450
Oxidation by OH	600	600	1200
Total	990	770	1760